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Electromagnetic interference shielding performance of epoxy composites filled with multiwalled carbon nanotubes/manganese zinc ferrite hybrid fillers

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ABSTRACT

An effective electromagnetic-interference (EMI) shielding epoxy composite has been fabricated with a combination of multiwalled carbon nanotubes (MWCNTs) and manganese zinc ferrite (MnZn ferrite) fillers. MWCNTs were functionalized to improve dispersibility while manganese zinc ferrite nanoparticles were synthesized via the citrate gel method. The EMI-shielding performance of the fabricated composites was examined. It was found that the composite with a filler ratio of MWNCTs to MnZn ferrite = 3:1 obtained the highest EMI shielding effectiveness (SE), with the shielding mechanism dominated by absorption. In addition, the EMI shielding performance of composites was improved by increases in the filler loading and thickness of composites. Composites with a filler loading of 4.0 vol% and thickness of 2.0 mm achieved an SE of 44 dB at 10 GHz with the assistance of conductive silver backing. This EMI SE is better than that of composites filled with single conductive filler and comparable with that of commercial EMI absorber.

1. Introduction

The electromagnetic interference (EMI) problem is getting serious due to increase in sensitivity of electronic devices, since currently most electronic gadgets are wireless and higher chip speeds [1,2]. Thus, an effective method of providing shielding from unwanted electromagnetic waves is in strong demand. The primary mechanism of conductive EMI shielding is usually reflection [3]. However, the reflected wave will bring "secondary electromagnetic pollution" to the surroundings. In order to obtain low reflection of the shield, impedance matching between the shield and free space is crucial [4].

Recently, a new strategy for providing EMI shielding was implemented by introducing both dielectric and magnetic lossy nanofillers into composites to give a very effective EMI absorption in a broad frequency range with controllable permittivity and permeability of composites [5,6]. Carbon nanotubes are widely used as an EMI shielding material due to their excellent dielectric properties, and they have demonstrated enhanced EMI attenuation when a low filler loading is embedded into a polymer matrix [7,8]. On the other hand, manganese zinc ferrite ($Mn_{1-x}Zn_xFe_2O_4$) is gaining popularity due to its fascinating magnetic and electromagnetic properties. It has good chemical stability, high permeability, high resistivity, and a large saturation magnetic flux density, which make it a good electromagnetic-wave absorber [9,10]. Therefore it can be foreseen that the combination of carbon nanotubes and manganese zinc ferrite filler will be able to improve the effectiveness of EMI shielding.

In the present work, EMI-shielding composites were obtained by mixing epoxy resin with hybrid fillers consisting of functionalized MWCNTs (F-MWCNTs) and manganese zinc ferrite nanoparticles. MWCNTs were functionalized with nitric acid for controlled formation of the functional group with better dispersibility, while manganese zinc ferrite nanoparticles were synthesized by the citrate gel method. The effect of the hybrid filler ratio, filler loading, and thickness of composites on the shielding effectiveness (SE) was investigated, and the EMI-shielding mechanism of these EMI-shielding composites is discussed.

2. Materials and methods

2.1. Materials

MWCNTs were purchased from USAINS Holding, Universiti Sains, Malaysia. These MWCNTs were produced via a catalytic

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chemical vapor deposition process, with carbon purity of more than 80% [11]. The average diameter and average length of MWCNTs were 10 ± 1 nm and 1–5 µm, respectively. Residuals of the MWCNTs may include molybdenum and cobalt. The precursors used for MnZn ferrite synthesis were iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, analytical grade), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%), and manganese (II) nitrate hexahydrate ($Mn(NO_3)_2 \cdot 6H_2O$, $>98\%$). All three precursors were purchased from Acros Organics BVBA. The chelating agent citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, analytical grade) was purchased from Fisher Scientific. Epoxy resin used in this research was D.E.R. 332 Epoxy Resin, a bisphenol A diglycidylether (DGEBA), with an epoxide equivalent weight of 171–175 g/eq. Epoxy resin was supplied by Penchem Technologies Sdn. Bhd. Polyetheramine D230 M was used as a hardener in this study. Here, the mixing ratio was set to 100 epoxy resin to 32 hardener. Also, 65% nitric acid for analysis (max.: 0.005 ppm Hg) EMSURE ISO was purchased from Merck Millipore, 25% ammonia solution for analysis EMSURE was purchased from Merck Millipore, and CMOS grade acetone was purchased from JT Baker.

2.2. Functionalization of MWCNTs

The functionalization process used in this study was based on previous works [12–14]. However, modifications of process parameters and a pre-sonication step before reflux were considered in the present study. Here, 0.3 g of pristine MWCNTs was added to a 250 ml Pyrex round-bottomed flask containing nitric acid aqueous solution (65%). The mixture of MWCNTs and nitric acid was sonicated in a conventional ultrasonic bath (Sono Swiss SW12H) for an hour to promote disentanglement of MWCNTs within the acid solution. Next, the mixture was heated by a heating mantle under reflux at a temperature of 120 °C. After 2 h of reflux, the mixture was filtered using vacuum filtration with a 0.45 µm polytetrafluoroethylene (PTFE) membrane (Merck Millipore), and the filtration residue was rinsed with deionized water until all the nitric acid was neutralized. The functionalized MWNCTs (F-MWCNTs) were dried in a vacuum oven for 24 h at 80 °C.

2.3. Synthesis of manganese zinc ferrite

The experimental procedure for synthesis of manganese zinc ferrite (MnZn ferrite) is based on previous work [15]. However slight modification was done, where calcination was carried out in an inert environment without a further annealing step. In this method, first the precursors $Fe(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Mn(NO_3)_2 \cdot 6H_2O$ were dissolved in deionized water with respective stoichiometry under stirring. After all the metal nitrate precursors had dissolved, 10 ml of citric acid was added. The mole ratio of citric acid to total metal ions was controlled at 1:1. Ammonium hydroxide solution (NH_4OH) with a concentration of 0.10 mol/L was slowly added into the mixture in order to reach pH 5–7. Then the mixture was stirred at 30 °C for 24 h to complete the reaction. After 24 h of stirring, the solution was heated to 80 °C until gel formed. The produced gel was dried in an oven at 100 °C for 12 h. The final product was obtained after 2 h of calcination at 1000 °C in an argon atmosphere. X-ray diffraction analysis (shown in Fig. 1) was performed on the final product to confirm the presence of manganese zinc ferrite phase.

2.4. Sample preparation

The EMI-shielding composites were fabricated by the conventional casting method and the sample identification is described in Table 1. F-MWCNTs and synthesized MnZn ferrite were added to epoxy resin (D.E.R. 332). The mixture was sonicated with a sonicator (Hielscher – Ultrasound Technology, UP200S) at room temperature, for 10 min, with 50% amplitude and a 0.5 sonication cycle. Once the sonication process was completed, the curing agent (polyetheramine, D230 M) was added into the mixture at a ratio of 100:32 by weight (epoxy to curing agent). The mixture was immediately sonicated for another 10 min, in the presence of an ice-water bath, to slow down the curing process. After sonication, the mixture was placed in a vacuum oven (National Appliance Model 5831) for 45 min for the degassing process in order to remove the air entrapped during sonication. In the meantime, soapy water was applied to the glass mold as a releasing agent. Once the degassing process was finished, the mixture was poured into a glass mold and dried at room temperature for 12 h. Lastly, the composite sheet was cured at 80 °C for 2 h.

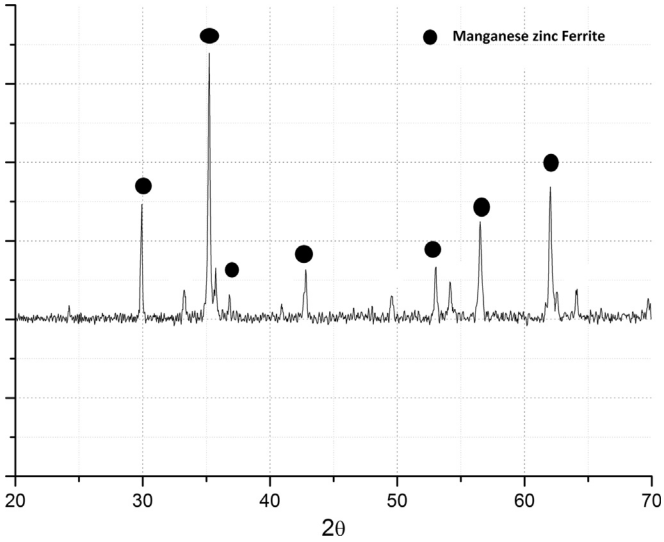

Fig. 1. The presence of manganese zinc ferrite phase found on synthesized ferrite powders by using X-ray diffraction analysis (XRD).

Table 1
Identification of fabricated EMI-shielding composites.

Sample Name	Fillers
C 100	100 vol% MWNCTs
C75F25	75 vol% MWNCTs + 25 vol% MnZn ferrite
C50F50	50 vol% MWNCTs + 50 vol% MnZn ferrite
C25F75	25 vol% MWNCTs + 75 vol% MnZn ferrite
F100	100 vol% MnZn ferrite

2.5. Characterization

The EMI-shielding effectiveness (SE) measurement method used in this study is a waveguide system with a measured frequency range of 7 to 12 GHz. This set-up was done according to previous work [16]. A vector network analyzer was connected to two coaxial-waveguide adapters. The composite was located between the adapters during the measurement. The incident and transmitted waves in a two-port vector network analyzer are mathematically represented by complex scattering parameters (or S-parameters). The S-parameters, S_{11} (or S_{22}) and S_{12} (or S_{21}) were correlated with reflectance (R) and transmittance (T), respectively, based on Eq. (1).

$$T = \left|\frac{E_T}{E_I}\right|^2 = |S_{12}|^2; R = \left|\frac{E_R}{E_I}\right|^2 = |S_{11}|^2 \tag{1}$$

The absorbance, A, was represented as $A = (1 - R - T)$. Once the transmittance and absorbance parameters had been obtained, the